

DNAPL Panel Session¹

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Panel Question 1: What metric should be used to evaluate the vertical and lateral extent of the source area?

Kueper: Recognize the need for converging lines of evidence. Examine the site history, evaluate soil core data (both stratigraphic and chemical), and look at ground water concentrations using vertical and lateral profiles and trends. Examine head and flowpath data to create a complete flownet. If you cannot draw a vertical and horizontal flownet at the site, then you have not properly characterized it. The presence of alcohols can also indicate DNAPL presence. They are generally very mobile, and if they are still around, then they are likely to be slowly partitioning out of a source zone. Recognize that even with the best data collection effort there will still be uncertainty in the exact boundaries of a DNAPL zone.

Cummings: At the Ft. Lewis site, investigators used a CPT/LIF rig, which has been used at a number of wood treater sites. The wavelengths available are not very effective for tar-like materials, however, and can only detect chlorinated aliphatics if they are mixed with oils containing two- and three-ring polynuclear aromatics. There is a new probe available that identifies total halogenated hydrocarbons. This probe has the detector positioned downhole, which gives better vertical resolution.

Guswa: The thought process used to evaluate data is important. You need to know how the contaminants are likely to move in the subsurface so you can combine stratigraphic information with the ground-water concentrations and draw conclusions.

Panel Question 2: Given the difficulty in determining the vertical and lateral extent of the DNAPL source area, how close should you locate the containment system to the estimated source area?

Guswa: A physical barrier can be closer to the suspected source area than a hydraulic one because a hydraulic barrier runs the risk of increasing the DNAPL mobility. How close a barrier can be is site specific. The designer needs to consider the likelihood that some DNAPL may end up on the wrong side of the barrier and what the consequences will be. Also, the designer needs to consider how good the characterization of the DNAPL zone is, and we need to remember that most sites have some physical constraints on where barriers can be placed.

Kueper: Solid barriers are expensive, so there is a lot of interest in keeping physical barriers as small as possible. On the other hand, if you bisect the source with the barrier there could be financial consequences as well. With hydraulic system failure, there is some room for adjustment and there really is no need to put the pumping system close to the source to control offsite migration of the dissolved plume. The hydraulic approach allows for more flexibility.

¹The following write-up is a summary, not a transcript, of the panel session discussions.

Rao: Yes, but pump and treat is more expensive than a barrier in the long term, especially considering O&M costs.

Comment from the Audience: That is true. But when negotiating with PRPs, the issue is not money spent over 30 years and the savings a wall might provide. The issue is the amount of money spent now. The money spent this year counts; the savings over 30 years do not.

Cummings: Do not equate pump and treat of the dissolved phase with containment of the free phase. This is especially true at wood treating sites where the DNAPL is probably still moving.

Guswa: You need to examine the purpose of the containment system and the placement of the wells. If the purpose is to capture the dissolved phase only, then the well placement will not be conducive to capturing DNAPL or ensuring it is not moving. If you properly position the recovery wells and maintain a sufficiently high gradient, you can prevent further DNAPL migration. Pump and treat wells can be effective barriers depending on the density of the DNAPL.

Question from the Audience: Shouldn't you be more careful with the placement of pumping wells? Couldn't you move the DNAPL towards them?

Kueper: Our point is to illustrate the relative flexibility of barriers and hydraulic containment—not imply that well placement is not important. You can place the pumping wells just inside the DNAPL source area (ensuring that they are not screened below the base of the mass) and induce a sufficient gradient to capture the dissolved and free phases. Alternatively, you can place wells far enough outside the source that they only draw on the dissolved phase and don't affect the DNAPL. Placing the wells close to but not in the DNAPL zone might move the free phase in undesired ways.

Panel Question 3: What are the critical parameters that should be determined before designing a source area action?

Davis: For thermal treatment, the first parameter to determine is the volatility of the contaminant(s). For complex mixtures like wood treating creosotes, which may have varying amounts of compounds such as naphthalene and phenanthrene, it is necessary to know the composition of the DNAPL. In terms of the site hydrogeology, heterogeneity plays a big role—not so much in preventing or allowing use of thermal remediation—but in how the approach is designed. Thermal remediation has had reasonable success in all types of subsurfaces, including fractured rock at Loring Air Force.

Huling: It must first be known that the target contaminant is reactive with the oxidant. Knowing exactly where the source is located is important with in-situ chemical oxidation. There are several approaches to site characterization that could be used to accomplish this task, geophysical methods (membrane interface probe, etc.), and soil core and/or ground water sampling and analysis. The Waterloo Profiler™ is one method that can obtain closely spaced, discrete, dissolved-phase concentrations in the source area or downgradient of a DNAPL source. Ground-water concentrations represent an integrated measure of contaminants in the subsurface (source area) and are an excellent surrogate for free-phase or sorbed DNAPL masses which are traditionally more costly and difficult to characterize. The results from the Waterloo Profiler™ transects can be used to plan where chemical oxidation should be implemented or where to use continuous DP soil coring to look for DNAPL or high concentrations of sorbed contaminants in aquifer materials. The actual locations of the coring points can be selected randomly or biased depending upon the degree of information available about the site geology. Dr. Beth Parker (University of Waterloo) used a similar approach at a site in Fort Lauderdale and was very successful in identifying thin zones of contamination.

Question from the Audience: Do vendors consider the naturally occurring chemical oxygen demand?

Huling: No vendor or consultant would likely base their calculations of the amount of oxidant needed solely on the estimated DNAPL mass. We have known for quite some time the significant difficulty and uncertainties that exist with estimating contaminant mass. Additionally, they would have to consider background oxidant demand as well. The background oxidant demand can be and often is greater than the demand imposed by the target contaminant itself. Since there is always some uncertainty in the representativeness of background measurements, a safety factor should be added to ensure that sufficient oxidant is added to do the job. For example, there are numerous reasons why contaminant rebound will occur. This is why it is important to plan and budget for long term ground water monitoring and multiple applications of the oxidant reagents.

Annable: For in-situ flushing, it is important to know if DNAPL is present and its vertical and lateral extent. It is not quite as critical to know how much is present because the decision to stop a flush is based on the concentrations measured in the recovered flushing fluids, not a pre-calculated mass. The vertical extent and its relation to the hydrogeologic construct are very important for minimizing the potential for vertical migration. The locations of preferential pathways are also important for designing the flood. The physical and chemical properties of the in-situ DNAPL are useful for evaluating how different surfactants or solvents will react to them. Hence, some effort should be made to obtain cores with DNAPL in them. If sufficient DNAPL can be collected, laboratory column studies can be conducted to model how successful the flood may be.

Rao: You will also need to know how the flushing materials will react with both the aquifer matrix and the DNAPL. Will there be a change in the matrix? For example, strong adsorption of the surfactant could happen, and this in turn may make the NAPL the wetting agent instead of water.

Question from the Audience: So to what extent do you need to know the mass of the DNAPL?

Davis: The more important consideration for these technologies is the areal extent of the DNAPL. Knowing the volume of the DNAPL is generally more important for planning what to do with it when it is brought to the surface. There are instances where the surface treatment system was overwhelmed by the volume and concentrations recovered.

Huling: Estimating the volume or mass of the DNAPL is not that important to oxidation, mainly because of the complexity and uncertainties in accomplishing such a task. More important is the general magnitude of the mass because permanganate and Fenton's reagent work mainly in the aqueous phase and sites which contain massive quantities of DNAPLs could therefore be significantly challenging. If large quantities of DNAPL are present, it is probably better to consider in-situ flushing or thermal technologies to recover it, rather than trying to destroy it in place with chemical oxidation.

Question from the Audience: Is it better to use thermal remediation or in-situ flushing to remove the mass and use oxidation as a polishing step?

Huling: This could probably be used but it is not that straightforward. If thermal remediation is used to eliminate NAPLs, it is doubtful that chemical oxidation would be needed as a polishing step mainly due to the level of treatment accomplished. However, this should be assessed on a site specific basis because of some of the assumptions I've made. This approach could also be excessively expensive because of the volume of the flushing fluids, thermal energy, or oxidant reactants required. There are also technical issues, such as whether the amount of permanganate needed to oxidize the remaining material (solvent, DNAPL, etc.) could fill the voids in the aquifer matrix with manganese dioxide precipitate. So before deciding to use oxidation as a polish, you need to evaluate how much of the material is left, in what form,

and where. You also need to determine the amount of oxidant required, its expense, and whether it is technically feasible to treat what is left with oxidation.

Sorenson: For any of these technologies, you need to have an idea of the location (lateral and vertical extent) and the strength of the source. Like oxidation, biodegradation can not be used to treat large pools of DNAPL. To evaluate whether biodegradation is an option, you need to understand the biochemistry of the site, and the biochemistry can be understood using the monitored natural attenuation (MNA) protocols. Microcosms to evaluate whether or not a biodegradation remedy will work at a site are not necessarily representative of the entire site since rates can be very heterogeneous. The data from a good MNA evaluation are often more valuable than the data from a microcosm study. To determine if a site is going to be biologically limited, the microbial population must be characterized to understand where the degradation process will stop. For example, will the biodegradation process of PCE proceed to ethene or will it stop at DCE? If there is a complete suite of degradation products in the ground-water samples, then the answer is yes, it will proceed to ethene. If there is not a complete suite of products, the reason must be determined (e.g., carbon limited, biological limitation, or redox limitation). The methods for evaluating the causes have a number of uncertainties.

Question from the Audience: How often do you cost effectively locate the source of TCE plumes, and do all TCE-related plumes have sources?

Kueper: If there is a plume present, there probably is a source term as well. The source might not be very large, and there are examples where it has dissipated. However, given the expected longevity of the pure chemical in the ground, sites that do not have any DNAPL source will be rare. The primary reason that DNAPL sources are not found is because they are not actively pursued.

Sorenson: This is true for TCE plumes. If the head of the plume is not moving, there is a continuing source present. On the other hand, the source is weak at a number of sites, and as a result, many of the characterization techniques in use will not find it. The issue at these sites then becomes whether the exact location of the source is needed or whether the general area from which the high dissolved-phase concentrations are coming will suffice. For the most part, the general area—combined with a good understanding of the hydrogeology—will allow for a cost-effective estimate of the soil volume requiring treatment.

Guswa: We know that small volumes of DNAPL can give rise to large plumes, and many of the solvent plumes we encounter today are at small manufacturing plants that did not use a large volume of solvent. The source areas at such locations may be residual, which can still cause a big problem.

Panel Question 4: What is it that gives you a higher level of confidence or a lower level of confidence that your barrier will prevent the DNAPL from moving?

Guswa: Ideally, the aquitard at the site will be thick and have a low permeability, and the aquifer will have a low hydraulic gradient. This is rarely the case, however. There is typically less attention paid to verifying that the bottom of a barrier is competent and will maintain its integrity during construction. It is also important to evaluate whether the DNAPL has stopped moving, what caused it to stop moving, and whether it can be moved in the future.

Panel Question 5: At a wood treatment site where the DNAPL has migrated 40 to 60 feet bgs and the aquifer lies several hundred feet below, are there tools to predict when and if a DNAPL will impact the aquifer?

Kueper: You should assume that the DNAPL is still moving at a creosote or coal tar site, unless you can prove otherwise. You need to characterize the geology and determine what barriers exist and whether they are competent (e.g., Are the clay layers fractured?). On the other hand, it will take a long time for a creosote-type material to move through fractures, so you need to evaluate the fluid properties (e.g., chemical content, viscosity, and density) of the site-specific DNAPL. You probably should install some dry angle-drilled monitoring wells in the assumed path of the DNAPL mass. Even though they would be deep, it is also good to install some sentinel wells in the aquifer downgradient from the expected impact area. These wells should be adequately sized to accommodate a pump for pump and treat in case it is needed.

Question from the Audience: Once you find a source zone, how do you know that another source does not exist at greater depths? There are a number of cases where the suspected release volume is considerably larger than the volume that has been bounded. How do we reassure the public that we have indeed located all of the source areas?

Annable: Drilling deeper within a contaminated area is problematic because the source can be dragged down to greater depths. You do not have to introduce much DNAPL to greater depths to cause big problems.

Question from Moderator: Is it possible to sample deeper without dragging the shallower contamination down?

Annable: I am aware of a release due to a truck spill where emergency response personnel wanted to quickly see how deep the spill had penetrated. Instead of taking precautions, they drilled right through the material and carried it deeper, from 20 to 60 feet bgs. Dragdown doesn't have to happen though. Although slower and more expensive than traditional drilling methods, you can drill telescoped boreholes or wells by successively placing smaller casing within outer casing that has been grouted off to prevent material from migrating deeper along the sides of the borehole. In addition, you can use dual tube, direct push methods or dual tube drilling to accomplish the same thing.

Guswa: The technologies have improved for characterization beneath contaminated zones, and there is little chance of introducing large quantities of DNAPL into a clean subsurface if one anticipates and prepares for that possibility. However, it is possible to introduce a very small amount of DNAPL that does not pose a health risk, but will be sufficiently large to show up at low levels in ground-water samples. This will change your conceptual model and cause you to look for a source that is not there.

Rao: During characterization, you should also be aware of deeper dissolved plumes created by distant production wells that may be inducing a downward vertical gradient. Abandoned wells with extremely long screens may also cause a problem because they can act as conduits for the dissolved phase, especially in conjunction with active pumping wells.

Panel Question 6: What are the benefits of a costly, detailed profiling if the remedy will treat the entire volume?

Kueper: You need to know which end of the contaminant spectrum you are dealing with at a site—scattered residual or a massive pool—in order to select which technology or treatment train would be best. You don't want to choose oxidation or biodegradation when pools of DNAPL are present because these technologies would be inappropriate, and you won't know if pools are present without proper characterization.

Huling: The more discrete your characterization intervals are, the more you can target the correct zone with treatment. This will save money.

Rao: The knowledge of the contaminant architecture determines the remediation design. There are two issues: one is knowing the evolution of the plume and being able to evaluate remedy performance by how it changes the plume; and the second is that the target volume does not need to be treated uniformly. You are better off targeting specific zones, not an entire area, which allows for a more cost-effective treatment design.

Sorenson: For biodegradation, you do need to know whether a pool or residual is present. However, knowing the source architecture is not as important for biodegradation as other technologies. The considerations are somewhat different because biodegradation treats the aqueous phase, and the treatment zone needs to be somewhat larger than the source. Treatment also creates a relatively uniform biologically active area that should be effective for whatever dissolved materials pass through.

Question from the Audience: I have a wood treater with an estimated 1 million gallons of NAPL down to 220 feet, and it is still moving. The estimated cost for source remediation is very high. How can I determine how fast the NAPL is traveling? Could you explain how angled well screens would be applied?

Kueper: Rather than determining where the contamination is, determine where it is not. Instead of vertical profiling with point-in-time samplers, you will need permanently installed monitoring points in a downgradient clean zone (hydraulically and stratigraphically) to track the flux rate over time. Establishing monitoring points in the contaminated area will not answer the question of mobility. Also, consider drilling wells in the source area and pump them to both recover product and put a sufficient hydraulic gradient on the DNAPL to stop its movement.

Question from the Audience: Dr. Huling mentioned the limitations of permanganate for treating residual DNAPL. Are there any such limitations for using persulfate to treat residual DNAPL?

Huling: Persulfate is an experimental oxidant that has some applications. The first thing to do is to make sure the target compound can be transformed by persulfate in the lab, because there are a suite of compounds that are not vulnerable to persulfate oxidation. Also, consider the temperature of the contaminated environment because persulfate is not significantly reactive at low temperatures.

Question from the Audience: Does persulfate have a crusting effect similar to permanganate?

Huling: Again, persulfate oxidation is an experimental technology, and there are still fundamental issues that are currently being investigated. This possibility should be tested in the laboratory.

Question from the Audience: How often is DNAPL mobilized downward as a result of remediation efforts? This potential has been used as an excuse to avoid any source remediation.

Davis: I am not aware of any case where downward mobilization has happened where thermal remediation was used. You can always use engineering controls to minimize the possibility of this occurring.

Cummings: At the six-phase heating demonstration at Cape Canaveral, there was an indication that the treatment drove some contaminants through the aquitard and into the underlying formation. The problem with the evaluation at this site was that there was no analysis for contamination in the underlying formation before the demonstration was executed, so it could have been a preexisting condition.

Question from the Audience: What about surfactants?

Kueper: If you lower the interfacial tension of a DNAPL pool and the pool is near its critical height, then it will move downward. If we understand the mechanisms of the downward mobilization, we can try to engineer countermeasures such as creating a hydraulic bottom using properly placed wells and appropriate pumping rates. I looked at 27 field trials of alcohols and surfactants several years ago and concluded that monitoring wells were not in place to assess downward movement. In fact, most trials did not even monitor downgradient water quality.

Annable: While it is hard to find the extent of the DNAPL source zone, it is even harder to determine whether it is moving. To prove that DNAPL is not moving is nearly impossible; to prove that it is moving, you have to show that it was not there to start with. The difficulty in monitoring DNAPL movement is probably the reason it isn't done. When you use technologies that reduce interfacial tension, the risk of downward movement is real. However, there are ways to counteract this movement.

Rao: What makes monitoring more difficult, in many cases, is that regulatory authorities do not allow monitoring below the mass. You may be able monitor following treatment, but by then you can't prove whether contamination was there before or as a result of remedial activities. You can also monitor changes in the water quality of deeper ground-water monitoring wells, which would indicate a new source.

Sorenson: Vertical profiling of the ground-water quality should be done before and after a surfactant flood to determine whether DNAPL has moved. The post-flood profile should be conducted long enough after the flood to allow any new dissolved phase to reach it.

Rao: You should always have a monitoring well system set up to measure changes in the dissolved plume composition and architecture (both vertically and horizontally) if for no other reason than to measure remedial performance and decide future actions, if necessary.

Question from the Audience: There are a lot of sites in Texas where creosote has moved downward through fractured clays and sands to great depths. What remedies do you recommend for this situation?

Kueper: If the goal is to stop the creosote from moving, you may be able to stop or reverse the flow with a sufficiently high hydraulic gradient. The downsides to this approach are that a lot of water must be treated and pumping must be continued in perpetuity. Another option is to try to remove a sufficient amount of the mass to stop it from flowing. Deep physical barriers are difficult to emplace, and DNAPL may bypass them.

Question from the Audience: Are you working on biodegradation of DNAPL sources other than TCE, such as coal tars, which will probably require aerobic conditions?

Sorenson: Most of our efforts have focused on chlorinated compounds, but most studies of coal tars and creosotes do seem to indicate that aerobic methods are more robust for these types of contaminants.

Question from the Audience: If you were to change the cleanup goal from achieving MCLs throughout the plume to shrinking the plume and achieving MCLs at some point in the plume, would that lead to more efforts at source removal?

Annable: If you move the MCL compliance point some distance downgradient, then you have a chance to establish a treatment zone for the plume, which would make source removal more effective. The relationship, however, between partial source removal and dissolved phase flux is not well understood.

Cummings: I've been discussing chronological-based RODs with several of the EPA regions. You don't have to give up the MCLs, you just have to be more reasonable about the time frame in which to achieve them. A knowledge gap exists in evaluating and predicting mass flux changes. For example, if partial source removal is accomplished, how does that affect future treatment needs? Will you be able to decrease the number of years required for pump and treat?

Question from the Audience: Isn't it understood that if your mass flux matched your assimilative capacity, then the plume would disappear?

Rao: If the assimilative capacity of the system exactly matched the flux coming off the source, the plume would still expand. You need to have *more* assimilative capacity than flux for the plume to shrink. How quickly this will occur is the question Jim Cummings is asking. The issue is establishing a regulatory plane some place downgradient, such as a property line, and deciding that we need to reduce the plume to some level before it passes this plane. To do this, you use a combination of source removal and a treatment zone to bring the contaminant flux to a level below the assimilative capacity of the system.

Cummings: Under this scenario the plume would eventually dissipate, and the O&M costs would be related to monitoring the treatment zone to ensure it remains effective and to adding amendments, as needed.

Question from the Audience: Do we have the tools to work in that context?

Rao: There are a collection of tools available to measure flux. If the flux can be measured at multiple control planes as has been done in Germany, we could establish the existing natural attenuation capacity. The link that we are seeking between the source discharge and the assimilative capacity can be done now using flux as a tool. If you assume that the integrated techniques in the German method are a means to measure flux, and if you accept the fact that flux decreases along the plume, then you can measure natural attenuation. This provides an average capacity, however, not local values. 40-50 of these tests have been done in Germany, and tests are planned in the United States. A guidance manual for the test is being produced by the Strategic Environmental Research & Development Program (SERDP).

Sorenson: At one site with a treatment train in Idaho, it was decided that if the flux from the source could be completely stopped, pump and treat would not be required for most of the 2-mile-long plume due to natural attenuation processes documented to be occurring. Using biodegradation in front of the source eliminated the flux, so they were allowed to cease pump and treat. If the source area had been stronger, they could have done a partial source removal to lower the flux and then used a second treatment technology, such as biodegradation, to attack the flux as it came off the remaining source. This approach can be used to cut back pump and treat costs, if not eliminate them.